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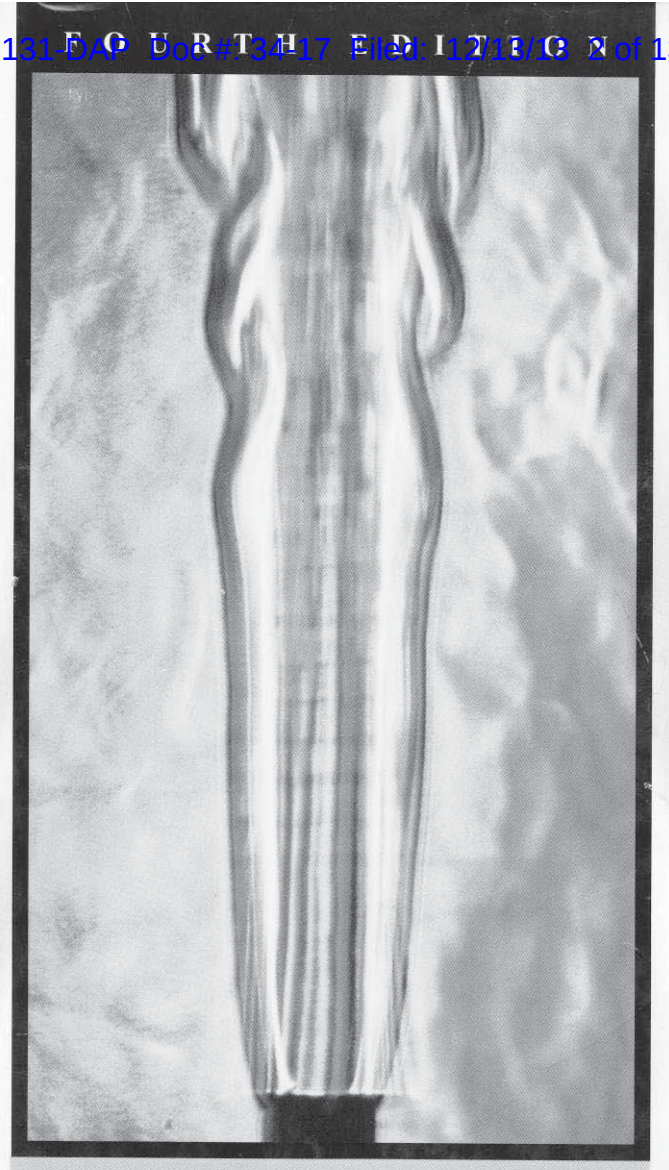

FOURTH EDITION

FUNDAMENTALS OF CLASSICAL THERMODYNAMICS

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ABOUT THE COVER The photograph on the cover of this textbook was taken by Professor Norman Chigier, William J. Brown Professor of Mechanical Engineering at Carnegie Mellon University. The high speed photograph is of a natural gas emerging from a nozzle and mixing with the surrounding air. The color photograph shows temperature variations and flow patterns. The highest temperature regions of the flame, around 2000K, are located where the air-fuel ratio is stoichiometric. The gas jet is initially laminar and becomes turbulent farther downstream. Entrainment of air from the surroundings can be seen to be associated with the engulfment of large vortex structures. The most luminous regions of the flame have solid carbon particles that radiate at high temperatures to the surroundings at lower temperatures. These carbon particles can be burnt in the flame in the presence of oxygen or emitted as smoke. Several hundred intermediate chemical reactions occur when methane and oxygen react in high temperature flames and cause ionization of the gas. High speed visualization of flame structures is leading to more detailed understanding of the chemical and physical processes of combustion.

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2 SOME CONCEPTS AND DEFINITIONS

One excellent definition of thermodynamics is that it is the science of energy and entropy. Since we have not yet defined these terms, an alternate definition in already familiar terms is: thermodynamics is the science that deals with heat and work and these properties of substances that bear a relation to heat and work. Like all sciences, the basis of thermodynamics is experimental observation. In thermodynamics these findings have been formalized into certain basic laws, which are known as the first, second, and third laws of thermodynamics. In addition to these laws, the zeroth law of thermodynamics, which in the logical development of thermodynamics precedes the first law, has been set forth.

In the chapters that follow, we will present these laws and the thermodynamic properties related to these laws, and apply them to a number of representative examples. The objective of the student should be to gain both a thorough understanding of the fundamentals and an ability to apply these fundamentals to thermodynamic problems. The examples and problems further this twofold objective. It is not necessary for the student to memorize numerous equations, for problems are best solved by the application of the definitions and laws of thermodynamics. In this chapter some concepts and definitions basic to thermodynamics are presented.

2.1 A THERMODYNAMIC SYSTEM AND THE CONTROL VOLUME

A thermodynamic system is a device or combination of devices containing a quantity of matter that is being studied. To define this more precisely a control volume is chosen, so that it contains the matter and devices inside a control surface. Everything external to the control volume is the surroundings, with the separation given by the control surface. The surface may be open or closed to mass flows and it may have flows of energy in terms of heat transfer and work across it. The boundaries may be movable or stationary. In the case of a control surface that is closed to mass flow, so that no mass can escape or enter the control volume, it is called a **control mass** containing the same amount of matter at all times.

Selecting the gas in the cylinder of Fig. 2.1 as a control volume by placing a control surface around it, we recognize this as a control mass. If a Bunsen burner is placed under the cylinder, the temperature of the gas will increase and the piston will rise. As the piston rises, the boundary of the control mass moves. As we will see later, heat and

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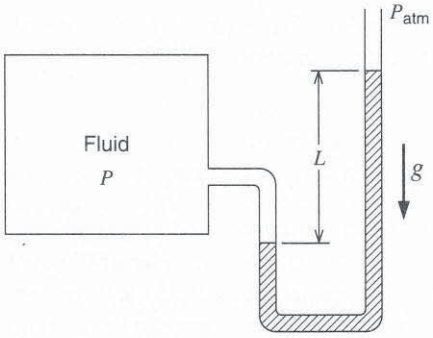

FIGURE 2.9 Example of pressure measurement using a column of fluid.

ples of hydrostatics one concludes that for a difference in level of L meters, the pressure difference in pascals is calculated by the relation

$$\Delta P = \rho L g$$

where ρ is the density of the fluid, and g is the local acceleration due to gravity. The accepted standard value for gravitational acceleration is

$$g = 9.806\,65 \text{ m/s}^2 = 32.174 \text{ ft/s}^2$$

but the value varies with location and elevation. The use of a manometer is illustrated in Fig. 2.9.

For distinguishing between absolute and gauge pressure in this text, the term pascal or lbf/in.^{2} will always refer to absolute pressure. Any gauge pressure will be indicated as such.

2.9 EQUALITY OF TEMPERATURE

Although temperature is a familiar property, an exact definition of it is difficult. We are aware of "temperature" first of all as a sense of hotness or coldness when we touch an object. We also learn early that when a hot body and a cold body are brought into contact, the hot body becomes cooler and the cold body becomes warmer. If these bodies remain in contact for some time, they usually appear to have the same hotness or coldness. However, we also realize that our sense of hotness or coldness is very unreliable. Sometimes very cold bodies may seem hot, and bodies of different materials that are at the same temperature appear to be at different temperatures.

Because of these difficulties in defining temperature, we define equality of temperature. Consider two blocks of copper, one hot and the other cold, each of which is in contact with a mercury-in-glass thermometer. If these two blocks of copper are brought into thermal communication, we observe that the electrical resistance of the hot block decreases with time and that of the cold block increases with time. After a period of time has elapsed, however, no further changes in resistance are observed. Similarly, when the blocks are first brought in thermal communication, the length of a side of the hot block decreases with time, but the length of a side of the cold block increases with time. After a period of time, no further change in length of either of the blocks is perceived. In addition, the mercury column of the thermometer in the hot block drops at first and that in the cold block rises, but after a period of time no further changes in height are observed. We

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may say, therefore, that two bodies have equality of temperature if, when they are in thermal communication, no change in any observable property occurs.

2.10 THE ZEROTH LAW OF THERMODYNAMICS

Now consider the same two blocks of copper and another thermometer. Let one block of copper be brought into contact with the thermometer until equality of temperature is established, and then remove it. Then let the second block of copper be brought into contact with the thermometer. Suppose that no change in the mercury level of the thermometer occurs during this operation with the second block. We then can say that both blocks are in thermal equilibrium with the given thermometer.

The zeroth law of thermodynamics states that when two bodies have equality of temperature with a third body, they in turn have equality of temperature with each other. This seems very obvious to us because we are so familiar with this experiment. Because the principle is not derivable from other laws, and because it precedes the first and second laws of thermodynamics in the logical presentation of thermodynamics, it is called the zeroth law of thermodynamics. This law is really the basis of temperature measurement. Every time a body has equality of temperature with the thermometer, we can say that the body has the temperature we read on the thermometer. The problem remains how to relate temperatures that we might read on different mercury thermometers or obtain from different temperature-measuring devices, such as thermocouples and resistance thermometers. This observation suggests the need for a standard scale for temperature measurements.

2.11 TEMPERATURE SCALES

Two scales are commonly used for measuring temperature, namely the Fahrenheit (after Gabriel Fahrenheit, 1686–1736) and the Celsius. The Celsius scale was formerly called the centigrade scale but is now designated the Celsius scale after Anders Celsius (1701–1744), the Swedish astronomer who devised this scale.

The Fahrenheit temperature scale is used with the English Engineering system of units, and the Celsius scale with the SI unit system. Until 1954 both of these scales were based on two fixed, easily duplicated points—the ice point and the steam point. The temperature of the ice point is defined as the temperature of a mixture of ice and water that is in equilibrium with saturated air at a pressure of 1 atm. The temperature of the steam point is the temperature of water and steam, which are in equilibrium at a pressure of 1 atm. On the Fahrenheit scale these two points are assigned the numbers 32 and 212, respectively, and on the Celsius scale the points are 0 and 100, respectively. Why Fahrenheit chose these numbers is an interesting story. In searching for an easily reproducible point, Fahrenheit selected the temperature of the human body and assigned it the number 96. He assigned the number 0 to the temperature of a certain mixture of salt, ice, and salt solution. On this scale the ice point was approximately 32. When this scale was slightly revised and fixed in terms of the ice point and steam point, the normal temperature of the human body was found to be 98.6 F.

In this text the symbols F and °C will denote the Fahrenheit and Celsius scales, respectively. The symbol T will refer to temperature on all temperature scales.

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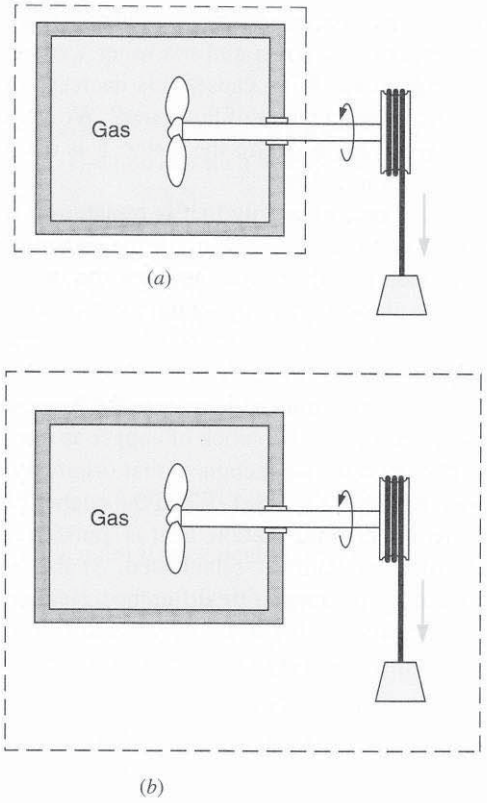

FIGURE 4.13 Example showing how selection of the system determines whether work is involved in a process.

tempted to calculate the work from the integral

$$\int_1^2 P\,dV$$

However, this is not a quasi-equilibrium process, and therefore the work cannot be calculated from this relation. Because there is no resistance at the system boundary as the volume increases, we conclude that for this system no work is done in this process of filling the vacuum.

Another example can be cited with the aid of Fig. 4.13. In Fig. 4.13*a* the system consists of the container plus the gas. Work crosses the boundary of the system at the point where the system boundary intersects the shaft, and can be associated with the shearing forces in the rotating shaft. In Fig. 4.13*b* the system includes shaft and weight as well as the gas and the container. Therefore, no work crosses the system boundary as the weight moves downward. As we will see in the next chapter, we can identify a change of potential energy within the system, but this should not be confused with work crossing the system boundary.

4.7 DEFINITION OF HEAT

The thermodynamic definition of heat is somewhat different from the everyday understanding of the word. It is essential to understand clearly the definition of heat given here, because it plays a part in so many thermodynamic problems.

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If a block of hot copper is placed in a beaker of cold water, we know from experience that the block of copper cools down and the water warms up until the copper and water reach the same temperature. What causes this decrease in the temperature of the copper and the increase in the temperature of the water? We say that it is the result of the transfer of energy from the copper block to the water. It is out of such a transfer of energy that we arrive at a definition of heat.

Heat is defined as the form of energy that is transferred across the boundary of a system at a given temperature to another system (or the surroundings) at a lower temperature by virtue of the temperature difference between the two systems. That is, heat is transferred from the system at the higher temperature to the system at the lower temperature, and the heat transfer occurs solely because of the temperature difference between the two systems. Another aspect of this definition of heat is that a body never contains heat. Rather, heat can be identified only as it crosses the boundary. Thus, heat is a transient phenomenon. If we consider the hot block of copper as one system and the cold water in the beaker as another system, we recognize that originally neither system contains any heat (they do contain energy, of course). When the copper block is placed in the water and the two are in thermal communication, heat is transferred from the copper to the water until equilibrium of temperature is established. At this point we no longer have heat transfer, because there is no temperature difference. Neither of the systems contains heat at the conclusion of the process. It also follows that heat is identified at the boundary of the system, for heat is defined as energy being transferred across the system boundary.

4.8 UNITS OF HEAT

Heat, like work, is a form of energy transfer to or from a system. Therefore, the units for heat, and to be more general, for any other form of energy as well, are the same as the units for work, or are at least directly proportional to them. In the International System the unit for heat (energy) is the joule. Similarly, in the English System, the foot pound force is an appropriate unit for heat. However, another unit came to be used naturally over the years, the result of an association with the process of heating water, such as that used in connection with defining heat in the previous section. Consider as a system 1 lbm of water at 59.5F. Let a block of hot copper of appropriate mass and temperature be placed in the water, so that when thermal equilibrium is established the temperature of the water is 60.5F. This unit amount of heat transferred from the copper to the water in this process is called the British thermal unit (Btu). More specifically, it is called the 60-degree Btu, defined as the amount of heat required to raise 1 lbm of water from 59.5F to 60.5F. (The Btu as used today is actually defined in terms of the standard SI units.) It is worth noting here that a unit of heat in metric units, the calorie, originated naturally in a manner similar to the origin of the Btu in the English system. The calorie is defined as the amount of heat required to raise 1 gram of water from 14.5°C to 15.5°C.

Heat transferred *to* a system is considered positive, and heat transferred *from* a system is negative. Thus, positive heat represents energy transferred to a system, and negative heat represents energy transferred from a system. The symbol Q represents heat. A process in which there is no heat transfer ($Q = 0$) is called an adiabatic process.

From a mathematical perspective, heat, like work, is a path function and is recognized as an inexact differential. That is, the amount of heat transferred when a system undergoes a change from state 1 to state 2 depends on the path that the system follows during the change of state. Since heat is an inexact differential, the differential is written δQ.

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On integrating, we write

$$\int_1^2 \delta Q = {}_1Q_2$$

In words, ${}_1Q_2$ is the heat transferred during the given process between states 1 and 2.

The rate at which heat is transferred to a system is designated by symbol $\dot{Q}$.

$$\dot{Q} \equiv \frac{\delta Q}{dt}$$

It is also convenient to speak of the heat transfer per unit mass of the system, q, often termed "specific heat transfer," which is defined as

$$q \equiv \frac{Q}{m}$$

4.9 COMPARISON OF HEAT AND WORK

At this point it is evident that there are many similarities between heat and work.

1. Heat and work are both transient phenomena. Systems never possess heat or work, but either or both cross the system boundary when a system undergoes a change of state.
2. Both heat and work are boundary phenomena. Both are observed only at the boundaries of the system, and both represent energy crossing the boundary of the system.
3. Both heat and work are path functions and inexact differentials.

It should also be noted that in our sign convention, $+Q$ represents heat transferred *to* the system and thus is energy added to the system, and $+W$ represents work done *by* the system and thus represents energy leaving the system.

A final illustration may help explain the difference between heat and work. Figure 4.14 shows a gas contained in a rigid vessel. Resistance coils are wound around the outside of the vessel. When current flows through the resistance coils, the temperature of the gas increases. Which crosses the boundary of the system, heat or work?

In Fig. 4.14*a* we consider only the gas as the system. The energy crosses the boundary of the system because the temperature of the walls is higher than the temperature of the gas. Therefore, we recognize that heat crosses the boundary of the system.

In Fig. 4.14*b* the system includes the vessel and the resistance heater. Electricity crosses the boundary of the system, and as indicated earlier, this is work.

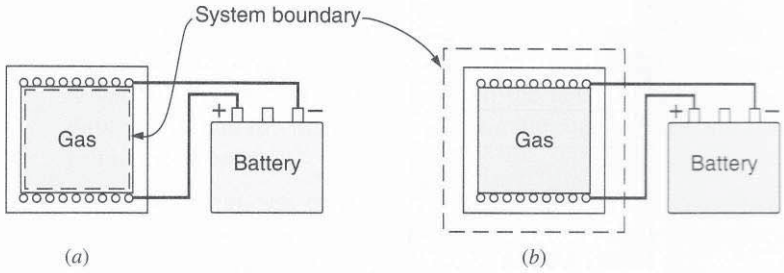

FIGURE 4.14 An example showing the difference between heat and work.

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6 THE SECOND LAW OF THERMODYNAMICS

The first law of thermodynamics states that during any cycle that a system undergoes, the cyclic integral of the heat is equal to the cyclic integral of the work. The first law, however, places no restrictions on the direction of flow of heat and work. A cycle in which a given amount of heat is transferred from the system and an equal amount of work is done on the system satisfies the first law just as well as a cycle in which the flows of heat and work are reversed. However, we know from our experience that because a proposed cycle does not violate the first law does not ensure that the cycle will actually occur. It is this kind of experimental evidence that led to the formulation of the second law of thermodynamics. Thus, a cycle will occur only if both the first and second laws of thermodynamics are satisfied.

In its broader significance the second law acknowledges that processes proceed in a certain direction but not in the opposite direction. A hot cup of coffee cools by virtue of heat transfer to the surroundings, but heat will not flow from the cooler surroundings to the hotter cup of coffee. Gasoline is used as a car drives up a hill, but the fuel level in the gasoline tank cannot be restored to its original level when the car coasts down the hill. Such familiar observations as these, and a host of others, are evidence of the validity of the second law of thermodynamics.

In this chapter, we consider the second law for a system undergoing a cycle, and in the next two chapters we extend the principles to a system undergoing a change of state and then to a control volume.

6.1 HEAT ENGINES AND REFRIGERATORS

Consider the system and the surroundings previously cited in the development of the first law, as shown in Fig. 6.1. Let the gas constitute the system and, as in our discussion of the first law, let this system undergo a cycle in which work is first done on the system by the paddle wheel as the weight is lowered. Then let the cycle be completed by transferring heat to the surroundings.

We know from our experience that we cannot reverse this cycle. That is, if we transfer heat to the gas, as shown by the dotted arrow, the temperature of the gas will increase, but the paddle wheel will not turn and raise the weight. With the given surroundings (the container, the paddle wheel, and the weight) this system can operate in a cycle in which the heat transfer and work are both negative, but it cannot operate in a cycle in which both the heat transfer and work are positive, even though this would not violate the first law.

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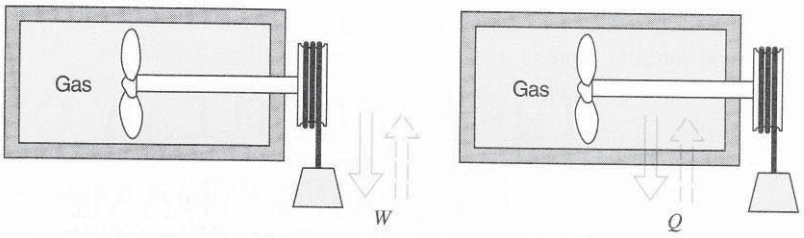

FIGURE 6.1 A system that undergoes a cycle involving work and heat.

Consider another cycle, which we know from our experience is impossible actually to complete. Let two systems, one at a high temperature and the other at a low temperature, undergo a process in which a quantity of heat is transferred from the high-temperature system to the low-temperature system. We know that this process can take place. We also know that the reverse process, in which heat is transferred from the low-temperature system to the high-temperature system, does not occur, and that it is impossible to complete the cycle by heat transfer only. This impossibility is illustrated in Fig. 6.2.

These two examples lead us to a consideration of the heat engine and the refrigerator, which is also referred to as a heat pump. With the heat engine we can have a system that operates in a cycle and performs a net positive work and a net positive heat transfer. With the heat pump we can have a system that operates in a cycle and has heat transferred to it from a low-temperature body and heat transferred from it to a high-temperature body, though work is required to do this. Three simple heat engines and two simple refrigerators will be considered.

The first heat engine is shown in Fig. 6.3. It consists of a cylinder fitted with appropriate stops and a piston. Let the gas in the cylinder constitute the system. Initially the piston rests on the lower stops, with a weight on the platform. Let the system now undergo a process in which heat is transferred from some high-temperature body to the gas, causing it to expand and raise the piston to the upper stops. At this point the weight is removed. Now let the system be restored to its initial state by transferring heat from the gas to a low-temperature body, thus completing the cycle. Since the weight was raised during the cycle, it is evident that work was done by the gas during the cycle. From the first law we conclude that the net heat transfer was positive and equal to the work done during the cycle.

Such a device is called a heat engine, and the substance to which and from which heat is transferred is called the working substance or working fluid. A heat engine may be defined as a device that operates in a thermodynamic cycle and does a certain amount of net positive work through the transfer of heat from a high-temperature body and to a low-temperature body. Often the term heat engine is used in a broader sense to include all devices that produce work, either through heat transfer or through combustion, even though the device does not operate in a thermodynamic cycle. The internal combustion

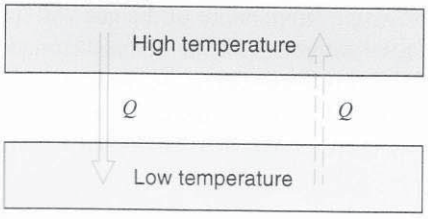

FIGURE 6.2 An example showing the impossibility of completing a cycle by transferring heat from a low-temperature body to a high-temperature body.

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perature body to a high-temperature body.

The thermoelectric refrigerator, which was discussed in Chapter 1 and is shown schematically in Fig. 1.9, is another example of a device that meets our definition of a refrigerator. The work input to the thermoelectric refrigerator is in the form of electrical energy, and heat is transferred from the refrigerated space to the cold junction (Q_L) and from the hot junction to the surroundings (Q_H).

The "efficiency" of a refrigerator is expressed in terms of the coefficient of performance, which we designate with the symbol β. For a refrigerator the objective, that is, the energy sought, is Q_L, the heat transferred from the refrigerated space. The energy that costs is the work W. Thus, the coefficient of performance, β,[1] is

$$\beta = \frac{Q_L(\text{energy sought})}{W(\text{energy that costs})} = \frac{Q_L}{Q_H - Q_L} = \frac{1}{Q_H/Q_L - 1} \tag{6.2}$$

Before we state the second law, the concept of a thermal reservoir should be introduced. A thermal reservoir is a body to which and from which heat can be transferred indefinitely without change in the temperature of the reservoir. Thus, a thermal reservoir always remains at constant temperature. The ocean and the atmosphere approach this definition very closely. Frequently it will be useful to designate a high-temperature reservoir and a low-temperature reservoir. Sometimes a reservoir from which heat is transferred is called a source, and a reservoir to which heat is transferred is called a sink.

6.2 SECOND LAW OF THERMODYNAMICS

On the basis of the matter considered in the previous section, we are now ready to state the second law of thermodynamics. There are two classical statements of the second law, known as the Kelvin–Planck statement and the Clausius statement.

> ***The Kelvin–Planck statement:*** It is impossible to construct a device that will operate in a cycle and produce no effect other than the raising of a weight and the exchange of heat with a single reservoir.

This statement ties in with our discussion of the heat engine. In effect, it states that it is impossible to construct a heat engine that operates in a cycle, receives a given amount of heat from a high-temperature body, and does an equal amount of work. The

[1]It should be noted that a refrigeration or heat pump cycle can be used with either of two objectives. It can be used as a refrigerator, in which case the primary objective is Q_L, the heat transferred to the refrigerant from the refrigerated space. It can also be used as a heating system (in which case it is usually referred to as a heat pump), the objective being Q_H, the heat transferred from the refrigerant to the high-temperature body, which is the space to be heated. Q_L is transferred to the refrigerant from the ground, the atmospheric air, or well water. The coefficient of performance for this case, β′ is

$$\beta' = \frac{Q_H(\text{energy sought})}{W(\text{energy that costs})} = \frac{Q_H}{Q_H - Q_L} = \frac{1}{1 - Q_L/Q_H}$$

It also follows that for a given cycle,

$$\beta' - \beta = 1$$

Unless otherwise specified, the term coefficient of performance will always refer to a refrigerator as defined by Eq. 6.2.

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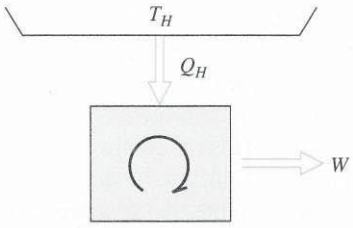

FIGURE 6.6 The Kelvin-Planck statement.

only alternative is that some heat must be transferred from the working fluid at a lower temperature to a low-temperature body. Thus, work can be done by the transfer of heat only if there are two temperature levels, and heat is transferred from the high-temperature body to the heat engine and also from the heat engine to the low-temperature body. This implies that it is impossible to build a heat engine that has a thermal efficiency of 100%.

> ***The Clausius statement:*** It is impossible to construct a device that operates in a cycle and produces no effect other than the transfer of heat from a cooler body to a hotter body.

This statement is related to the refrigerator or heat pump. In effect, it states that it is impossible to construct a refrigerator that operates without an input of work. This also implies that the coefficient of performance is always less than infinity.

Three observations should be made about these two statements. The first observation is that both are negative statements. It is of course impossible to "prove" a negative statement. However, we can say that the second law of thermodynamics (like every other law of nature) rests on experimental evidence. Every relevant experiment that has been conducted either directly or indirectly verifies the second law, and no experiment has ever been conducted that contradicts the second law. The basis of the second law is therefore experimental evidence.

A second observation is that these two statements of the second law are equivalent. Two statements are equivalent if the truth of each statement implies the truth of the other, or if the violation of each statement implies the violation of the other. That a violation of the Clausius statement implies a violation of the Kelvin–Planck statement may be shown. The device at the left in Fig. 6.8 is a refrigerator that requires no work and thus violates the Clausius statement. Let an amount of heat Q_L be transferred from the low-

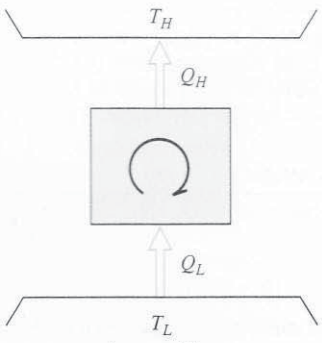

FIGURE 6.7 The Clausius statement.

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